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KINETICS OF SURFACE CHEMICAL REACTIONS

I. REACTION PROPAGATION FROM A PLANE SURFACE

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-USSR-

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FOREWORD

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KINETICS OF SURFACE CHEMICAL REACTIONS

I. REACTION PROPAGATION FROM A PLANE SURFACE

- USSR -

Following is a translation of the article entitled "Kinetika topokhimicheskikh reaktsiy I. Raspostraneniye reaktsii ot ploskoy poverkhnosti" (English version above) by O. M. Todes and R. I. Bogutskiy in Zhurnal Eksperimental'noy i Teoreticheskoy Fiziki (Journal of Experimental and Theoretical Physics), Vol 11, No 1, Moscow, 1941, pages 133-140.⁷

Contents: 1. Formulation of the problem and fundamental designations. -- 2. Kinetic equations of the process. -- A. Free growth of separate zones. -- B. Formation of the front. -- C. Linear velocity of the propagation of transformation. -- D. Complete form of curves (2) and (3). -- E. Position and magnitude of the maximum velocity for the general case. -- 3. Experimental determination of λ , n_0 , and a .

1. Formulation of the problem and fundamental designations.

We are going to investigate surface chemical reactions in solids, which do not take place simultaneously everywhere in the system, but begin in separate points of the solid, and from there spread throughout. The creation of "seeds" of "initiation centers" of a similar reaction may, as a function of conditions, take place in the interior, or on the surface of the solid, on the edges, ridges, or angles of the crystals.

The similar surface chemical reactions comprise:

1) the transformation of one solid phase into another -- recrystallization, and 2) the transformation of one solid body into another with the simultaneous evolution of a gaseous product, as is evidenced, for example, in the case of the decomposition of carbonates.

The theoretical analysis of the kinetics of similar reactions which are started on the crystal surface has encountered considerable difficulties arising from the fact, that the transformation zones which spread from the various "initiation centers" do not grow freely, but run across one another according to the conditions of the individual case. In the studies of Bradley, Colvin and Hume (1), Roginsky (2), Ismailow (3), and Yerofeyev (4), therefore, only separate and individual cases were investigated -- the beginning or the end of the process.

The example where the seeds of the new phase are formed in the interior of the original phases, according to the requirements of the case, but thereafter grow until mutual saturation was recently analyzed by Kolmogorov (5), and also by Johnson and Mehl (6) by some different methods. The conclusions of these authors represent some modification of a new method, which as far as we know was first suggested by Clausius during his determination of the laws of the partition of the free path.

We have accepted Clausius' method in the case of chemical reactions or phase transformations initiated on the surface of the solid. In this work we shall confine ourselves to the case of the plane surface, i.e., to particles of very large dimensions. The reaction kinetics for particles of ordinary dimensions, whose surface has a curvature different from zero, may be derived in a similar way.

The results of the latter investigation will be published by us separately.

For the analysis of the kinetics of the process for infinitely large particles, we will assume that from every center on the surface there spreads into the interior of the solid a spherical front of the process with a constant linear velocity λ cm/sec. The initiation centers of transformation may: 1) already at the very beginning of the process be found spread over the surface of the body at an average density n_0 per unit area, or 2) these centers are created as a function of time with an initial probability a per unit area per unit time interval. Naturally, a more complicated case is also possible, such that the transformation centers appear already on the surface partially formed as a function of time.

At the beginning of the process, the transformation

zones are uniformly growing hemispheres. As time goes on, these zones begin to interpenetrate one another, thus strongly complicating the kinetics of the process and its calculation. Eventually, after a sufficiently long period of time, all the separate zones merge and form one front of propagation of transformation, which travels in a direction perpendicular to the surface of the solid with the same linear velocity λ_0 .

The mathematical analysis of the kinetics of the initial period -- the period of free zone growth -- does not present particular difficulties. Depending on the nature of these initiation centers ($a = 0$, $n_0 \neq 0$, or $n_0 = 0$, $a \neq 0$) we obtain the yield of the reaction product proportional to the third or the fourth power of time t . The kinetics of the final stage is simpler still, where after the formation of a practically plane front, the quantity of the reaction product is directly proportional to t . The analysis of the intermediate period -- the interpenetration of zones and their merging into one front -- represents a fairly complicated problem in the theory of probability, which as yet has not been solved.

2. Kinetic equations of the process.

Considering the conversion of particles of sufficiently large dimensions, we may neglect the surface curvature and consider them as planes to all intents and purposes.

Thus, in the limiting case, one may consider the half-space bounded by the infinite plane, and filled with an isotropic, homogeneous substance, capable of undergoing a transformation.

At the interface we have, as before, transformation centers spread on the surface with an average surface density n_0 , according to the conditions of the case, and there may also be formed new centers, whose probability of formation, taken per unit area and unit time interval, we adopt as a .

Let us consider an arbitrary point M , which is at a distance x from the interface. We shall define the probability of the point M finding itself in a transformation zone at time t , which zone is propagated from some transformation centers on the surface, assuming that the transformation zone spreads from the center spherically with a constant linear velocity λ . Naturally, an inequality $t > x/\lambda$ is valid, as in the case of $t < x/\lambda$ the point M , in general, will not be in the reaction zone.

Thus, we will take $t > x/\lambda$ and investigate the time interval $(t, t + dt)$. Within this time interval, only those transformation zones may arrive at the point M which, firstly, propagate from transformation centers distributed with a surface density n_0 on the circumference of a circle of radius $r = \sqrt{\lambda^2 t^2 - x^2}$ with ring of width dr (figure 1); and secondly, from centers forming on rings, whose radii satisfy the condition $0 \leq r' \leq \sqrt{\lambda^2 t^2 - x^2}$ (figure 2), in the time interval dt , which is counted, however, not from time t , but from the moment $(t - \frac{1}{\lambda} \sqrt{r'^2 + x^2})$.

The probability of point M falling into the transformation zone during the time interval $(t, t + dt)$ will be equal to the sum of the probability of falling into the transformation zone propagating from centers distributed with a constant density n_0 .

$$p' = 2\pi n_0 r dr = 2\pi n_0 \lambda^2 t dt$$

and the probability of falling into the transformation zone propagating from centers during the time interval dt , but a little earlier is

$$p'' = dt \cdot 2\pi a \cdot \int_0^{\sqrt{\lambda^2 t^2 - x^2}} r' dr' = \pi a (\lambda^2 t^2 - x^2) dt.$$

The probability of the point M not undergoing transformation in the time interval $(t, t + dt)$ will be

$$q = 1 - (p' + p'') = 1 - [2\pi n_0 \lambda^2 t + \pi a (\lambda^2 t^2 - x^2)] dt.$$

However, the point M could have already experienced a transformation by time t . Assume $f(x, t)$ as the probability of the point M not being in transformation at time t , then the function $f(x, t + dt)$ is the probability of the point M not undergoing transformation at time $(t + dt)$.

It follows that we may write an equation

$$f(x, t + dt) = f(x, t) \{1 - [2\pi n_0 \lambda^2 t + \pi a (\lambda^2 t^2 - x^2)] dt\}.$$

Expanding the left-hand side into a power series in dt , we obtain an equation determining the unknown function $f(x, t)$:

$$\frac{df(x, t)}{f(x, t)} = -[2\pi n_0 \lambda^2 t + \pi a (\lambda^2 t^2 - x^2)] dt.$$

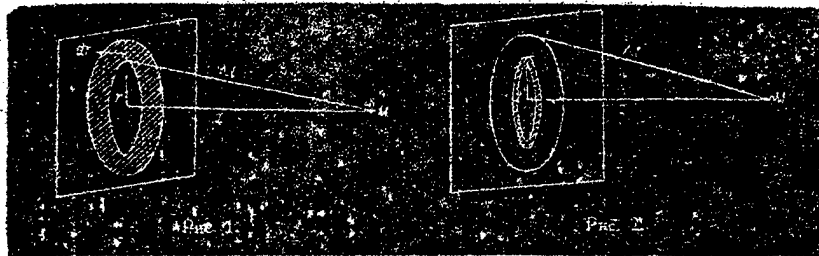


Fig. 1

Fig. 2

Solving the last equation, we will obtain an expression for $f(x, t)$:

$$f(x, t) = \exp[-\pi n_0 \lambda^2 (t^2 - x^2/\lambda^2) - \pi a (\frac{1}{3} \lambda^2 t^3 - x^2 t + \frac{2}{3} x^3/\lambda)] ,$$

in which the constant of integration is found from the obvious expression $f(x, x/\lambda) = 1$. We have obtained the probability of the point M not undergoing a transformation at time t . The probability of point M undergoing a transformation at time t will be

$$P(x, t) = 1 - f(x, t) = 1 - \exp[-\pi n_0 \lambda^2 (t^2 - x^2/\lambda^2) - \frac{\pi a \lambda^2}{3} (t^3 - 3tx^2/\lambda^2 + 2x^3/\lambda^3)] . \quad (1)$$

Let us distinguish an elementary layer of height dx and with base area of 1 cm^2 , in which point M is contained. The volume of the substance undergoing transformation in this layer at time t is equal to $P(x, t) \cdot 1 \text{ cm}^2 \cdot dx$, and the total volume experiencing transformation at time t , calculated for the unit surface area is:

$$v(t) = \int_0^{\lambda t} P(x, t) dx = \lambda t \left\{ 1 - \int_0^1 \exp[-\pi n_0 \lambda^2 t^2 (1 - z^2) - \frac{\pi a \lambda^2 t^3}{3} (1 - 3z^2 + 2z^3)] dz \right\} , \quad (2)$$

where $z = x/\lambda t$.

In the preceding discussion the quantity $P(x, t) \cdot 1 \text{ cm}^2 \cdot dx$ is identified with the portion of the

substance which at time t undergoes transformation in a volume of $1 \text{ cm}^2 \cdot dx$.

The transformation rate is

$$w(t) = \frac{dv(t)}{dt} = \lambda \left\{ 1 - \int_0^1 \exp[-\pi n_0 \lambda^2 t^2 (1 - z^2)] - \frac{\pi a \lambda^2 t^3}{3} \cdot (1 - 3z^2 + 2z^3) dz \right\} + \lambda t \left\{ 2\pi n_0 \lambda^2 t (1 - z^2) + \pi a \lambda^2 t^2 \cdot (1 - 3z + 2z^3) \right\} \exp[-\pi n_0 \lambda^2 t^2 (1 - z^2)] - \frac{\pi a \lambda^2 t^3}{3} \cdot (1 - 3z^2 + 2z^2) dz. \quad (3)$$

The evaluation of these integrals is not possible by conventional means, and it may be done approximately, only. It is expedient to analyze first the initial and the final parts of the process.

A. Free growth of separate zones.

In the initial part of the process, i.e., for small

t

$$t \ll \sqrt{\frac{1}{\pi n_0 \lambda^2}} = t_n, \quad \sqrt[3]{\frac{3}{\pi a \lambda^2}} = t_\alpha \quad (4)$$

one may expand the function under the integral sign in expression (2), limiting it to the first three terms. This approximation yields:

$$v(t) \approx \frac{2}{3} \pi n_0 \lambda^3 t^3 \left[1 - \frac{2}{5} \left(\frac{t}{t_n} \right)^2 \right] + \frac{\pi a \lambda^3 t^4}{6} \left[1 - \frac{13}{35} \left(\frac{t}{t_\alpha} \right)^3 \right] - \frac{13}{30} \lambda t \left(\frac{t}{t_n} \right)^2 \left(\frac{t}{t_\alpha} \right)^3. \quad (5)$$

The quantities $\frac{2}{3} \pi n_0 \lambda^3 t^3$ and $\frac{1}{6} \pi a \lambda^3 t^4$ give the sum of the volumes of all growth zones (hemisphere), formed between the time $t = 0$ and $t = t$, taken per unit area.

The multipliers $1 - \frac{2}{5} (t/t_n)^2$ and $1 - \frac{13}{35} (t/t_\alpha)^3$ afford a correction which takes into account, as a first approximation, the interpenetration of these zones; the quantity

$\frac{13}{30} \lambda t (t/t_n)^2 (t/t_\alpha)^3$ affords a correction which takes into

account, as a first approximation, the intersection of these zones which arise from centers of various types (distributed with a uniform density and in forming).

In the case of $n = 0$ or $a = 0$, we get

$$v(t) = \frac{\pi a \lambda^3 t^4}{6} \left[1 - \frac{13}{35} \left(\frac{t}{t_\alpha} \right)^3 \right]; \quad v(t) \approx \frac{2}{3} \pi n_0 \lambda^3 t^3 \left[1 - \frac{2}{5} \left(\frac{t}{t_n} \right)^2 \right]. \quad (6)$$

In the first case the initial growth of the product is proportional to t^4 , in the second case to t^3 .

B. The formation of the front.

For large times, when $t \gg t_n$ and t_α , the evaluation of the integral (2) may be effected by using the so-called "pass method", which takes advantage of the fact that the function under the integral sign is appreciably different from zero only in a small neighborhood of the point $z = 1$. Thus, we insert in the expression under the integral sign, $1 - z^2 \approx 2(1 - z)$, $1 - 3z^2 + 2z^3 \approx 3(1 - z)^2$ and we change the lower integration limit for an infinitely remote point. After some calculations, we obtain:

$$v(t) \approx \lambda t \left\{ 1 - \left[\frac{1}{2} \sqrt{\frac{\pi t_\alpha^3}{3t^3}} - \sqrt{\frac{t_\alpha^3}{3t^3}} \int_0^{t_n} e^{-z^2} dz \right] \exp\left(\frac{t_\alpha^3 t}{3t_n^4}\right) \right\}. \quad (7)$$

The integral in the last expression is equal, up to the limit of a constant, to the function of Kramp. As expression (7) is interesting only for large values of the argument, so using an asymptotic expression for the Kramp function, we obtain:

$$v(t) \approx \lambda t \left\{ 1 - \frac{1}{2} \left(\frac{t_n}{t} \right)^2 \left[1 - 1 \cdot \left(\frac{3t_n^4}{2t_\alpha^3 t} \right) + 1 \cdot 3 \left(\frac{3t_n^4}{2t_\alpha^3 t} \right) - \dots \right] \right\}. \quad (8)$$

From the latter it is seen that as time goes on, the expression in the brackets (curly) tends to unity, and $v(t) \rightarrow \lambda t$, i.e., a flat front is established, which spreads with a uniform linear velocity λ . In the case when

$$n_0 = 0, \text{ or } a = 0$$

$$v(t) \approx \lambda t - \frac{1}{2\sqrt{at}}; \quad (2)$$

$$v(t) \approx \lambda t - \frac{1}{2\pi n_0 \lambda t}.$$



Fig. 3

Expression (2) gives the linear velocity of propagation of the "average" front of transformation. In Figure 3 is shown the position of the average front for certain moments of time (dashed curves) and the position of the actual front for the same times (continuous curves).

We will calculate the magnitude of the velocity of propagation of transformation for the initial and final periods of the process. Differentiation of expression (2) with respect to time gives for $t \ll t_n$ and t_a :

$$w(t) \approx 2\pi n_0 \lambda^3 t^2 \sqrt{1 - \frac{2}{3} \left(\frac{t}{t_n} \right)^2} + \frac{2\pi a \lambda^3 t^3}{3} \sqrt{1 - \frac{15}{20} \left(\frac{t}{t_a} \right)^3} - \frac{2\pi}{3} \lambda \left(\frac{t}{t_n} \right)^2 \left(\frac{t}{t_a} \right)^2. \quad (10)$$

Correspondingly, for processes for which $n_0 = 0$, or $a = 0$:

$$w(t) \approx \frac{2\pi a \lambda^3 t^3}{3} \sqrt{1 - \frac{15}{20} \left(\frac{t}{t_a} \right)^3};$$

$$w(t) \approx 2\pi n_0 \lambda^3 t^2 \sqrt{1 - \frac{2}{3} \left(\frac{t}{t_n} \right)^2}. \quad (11)$$

For the final stage of the process, i.e., for $t \gg t_n$, and t_a :

$$w(t) \approx \lambda \sqrt{1 + \pi \left(\frac{t_n}{t} \right)^4 \left(1 - \frac{t_n^4}{t_a^4 t} + \frac{15}{6} \frac{t_n^6}{t_a^6 t^2} - \dots \right)}. \quad (12)$$

and, in the particular case when $n_0 = 0$, or $a = 0$

$$w(t) \approx \lambda + \frac{1}{4\sqrt{at^3}}; \quad w(t) \approx \lambda + \frac{1}{2\pi n_0 \lambda t^2}. \quad (13)$$

As is seen, for large times, the average front increases with a velocity slightly larger than λ . This is caused by the fact that the surface of the real front, to which the transformation propagates perpendicularly, is slightly larger than the area of the final plane front.

From formulas (10) and (12), and equally as well from figure 3, it is seen that the velocity $w(t)$ should attain a maximum value for some value of t .

D. Complete form of the curves (2) and (3).

Let us consider the complete form of the curves (2) and (3) for two particular cases: for $n_0 = 0$ and $a = 0$. In this investigation it is convenient to change over to dimensionless variables. Thus, we shall obtain universal curves, from which all experimental curves will be obtained for different a , n_0 , and λ by the mere change of scale. In the capacity of a time interval, we shall take the intervals introduced above t_α and t_n , during which time the front of the propagation of the transformation establishes itself. The natural scale for the velocity w is, of course, λ . Here also, the natural scale for the volume will be equal to λt_α , or λt_n , i.e., the volume

transforming per unit area in the time t_α and t_n , for the frontal propagation of transformation with the linear velocity.

Thus, for $n_0 = 0$, we introduce the dimensionless variables

$$\tau = \frac{t}{t_\alpha} = t \sqrt{\frac{3\pi a \lambda^2}{2}}; \quad f = \frac{v}{\lambda t_\alpha} = v \sqrt{\frac{3\pi a}{2}}; \quad w = \frac{w}{\lambda}, \quad (14)$$

where the expressions (2) and (3) in these variables are:

$$f(\tau) = \tau \left\{ 1 - \int_0^1 \exp[-\tau^3 (1-z)^2 (1+2z)] dz \right\}$$

$$w(\tau) = 1 - \int_0^1 \exp[-\tau^3 (1-z)^2 (1+2z)] dz +$$

$$3\tau^3 \cdot \int_0^1 (1-z)^2 (1+2z) \exp[-\tau^3 (1-z)^2 (1+2z)] dz. \quad (15)$$

The limit form of expression (15) with dimensionless variables will be:

$$\tau \ll 1; \quad f(\tau) \approx \frac{1}{2} \tau^4 (1 - \frac{13}{35} \tau^2); \quad w(\tau) = 2\tau^3 (1 - \frac{13}{20} \tau^2) \quad (16)$$

$$\tau \gg 1; \quad f(\tau) \approx \tau (1 - \sqrt{\pi/12} \tau^{-\frac{3}{2}});$$

$$w(\tau) = 1 + \sqrt{\pi/48} \tau^{-\frac{3}{2}}. \quad (17)$$

The result of the evaluation of the integral (15) for all values is shown in table 1; the corresponding curves are given in figures 4 and 5.

The velocity maximum lies at $\tau_m = 1.341$ and equals $w_m = 2.1331$.

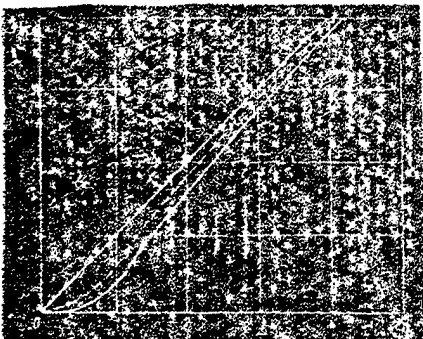


Fig. 4

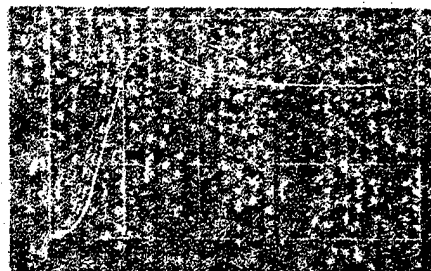


Fig. 5

For $a = 0$, introducing a dimensionless transformation

$$\theta = \frac{t}{t_n} = t \sqrt{\pi n_0} \lambda^2;$$

$$g = \frac{v}{\lambda t_n} = v \sqrt{\pi n_0}; \quad w = \frac{W}{\lambda}, \quad (18)$$

we obtain

$$g(\theta) = \theta \left\{ 1 - \int_0^1 \exp[-\theta^2(1-z^2)] dz \right\} \quad (19)$$

$$W(\theta) = 1 - \int_0^1 \exp[-\theta^2(1-z^2)] dz + 2\theta^2 \int_0^1 (1-z^2) \exp[-\theta^2(1-z^2)] dz \quad (20)$$

The limit values of the formulas (19) and (20):

$$\theta \ll 1; g(\theta) \approx \frac{2}{3}\theta^3(1 - \frac{2}{5}\theta^2); W(\theta) \approx 2\theta^2(1 - \frac{2}{3}\theta^2). \quad (21)$$

$$\theta \gg 1; g(\theta) \approx \theta - \frac{1}{2\theta}; W(\theta) = 1 + \frac{1}{2\theta^2}. \quad (22)$$

Results of the calculations of the integrals (19) and (20) are given in table 2. In this case the maximum velocity lies at $\theta_m = 1.500$ and is equal to $W_m = 1.285$.

TABLE 1

TABLE 2

TABLE 1				TABLE 2			
θ	$g(\theta)$	$W(\theta)$	$g'(\theta)$	θ	$g(\theta)$	$W(\theta)$	$g'(\theta)$
0.0	0.0000	0.0000	0.0000	1.0	0.4621	1.0775	0.4621
0.1	0.0007	0.0028	0.0007	1.1	0.5093	1.1217	0.5093
0.2	0.0028	0.0112	0.0028	1.2	0.5435	1.1618	0.5435
0.3	0.0063	0.0243	0.0063	1.3	0.5671	1.1983	0.5671
0.4	0.0112	0.0428	0.0112	1.4	0.5812	1.2310	0.5812
0.5	0.0180	0.0660	0.0180	1.5	0.5867	1.2500	0.5867
0.6	0.0265	0.0935	0.0265	1.6	0.5845	1.2565	0.5845
0.7	0.0365	0.1250	0.0365	1.7	0.5745	1.2500	0.5745
0.8	0.0480	0.1600	0.0480	1.8	0.5567	1.2310	0.5567
0.9	0.0600	0.1980	0.0600	1.9	0.5312	1.1983	0.5312
1.0	0.0725	0.2380	0.0725	2.0	0.4983	1.1618	0.4983
1.1	0.0850	0.2795	0.0850	2.1	0.4583	1.1217	0.4583
1.2	0.0965	0.3220	0.0965	2.2	0.4125	1.0775	0.4125
1.3	0.1070	0.3650	0.1070	2.3	0.3625	1.0283	0.3625
1.4	0.1165	0.4080	0.1165	2.4	0.3093	0.9750	0.3093
1.5	0.1250	0.4500	0.1250	2.5	0.2533	0.9183	0.2533
1.6	0.1325	0.4900	0.1325	2.6	0.1950	0.8583	0.1950
1.7	0.1390	0.5280	0.1390	2.7	0.1350	0.7950	0.1350
1.8	0.1440	0.5640	0.1440	2.8	0.0733	0.7283	0.0733
1.9	0.1475	0.5980	0.1475	2.9	0.0112	0.6583	0.0112
2.0	0.1500	0.6300	0.1500	3.0	0.0000	0.5850	0.0000

E. Position and magnitude of the velocity maximum for the general case.

We are investigating the change of the velocity as a function of time in two particular cases, have come to the conclusion that the velocity has a maximum, and have found its maximum.

It is interesting, now, to find out where this maximum velocity shall be found in the general case, and what its magnitude will be. For this, we will present

the integral (3) and its limit values (10) and (12) in the following form:

$$W(\chi) = 1 - \int_0^1 \exp[-\chi^2 \eta^2 (1-z^2) - \chi^3 (1-z)^2 (1+2z)] dz + \\ \int_0^1 [2\chi^2 \eta^2 (1-z^2) + 3\chi^3 (1-z)^2 (1+2z)] \exp[-\chi^2 \eta^2 (1-z^2) - \chi^3 (1-z)^2 (1+2z)] dz; \quad (23)$$

at $\chi \ll 1$

$$W(\chi) = 2\chi^2 \left[\left(1 - \frac{13}{20}\chi^3\right) + \eta^2 \left(1 - \frac{13}{10}\chi^3 - \frac{2}{3}\chi^2 \eta^2\right) \right] \quad (24)$$

at $\chi \gg 1$

$$W(\chi) = 1 + \frac{1}{2} \frac{1}{\chi^2 \eta^2} \left(1 - \frac{1}{\chi \eta^4} + \frac{135}{8} \frac{1}{\chi^2 \eta^8} - \dots\right), \quad (25)$$

where η is a dimensionless parameter

$$\eta = \sqrt[6]{9 \frac{\pi n_0^3 \chi^2}{a^2}} = \frac{t_\chi}{t_n}, \quad (26)$$

defining the relative density of center of the propagation of transformation (distributed with a uniform density with respect to formation in time). It is easily seen that the parameter η connects the dimensionless parameters introduced above χ and t , and especially $\chi = \chi(\eta)$.

The result of the calculation $\chi_m = \chi_m(\eta)$ and $W_m = W_m(\eta)$ is presented in table 3.

From table 3 it is seen that, if in addition to forming centers of transformation with constant probability of incidence a , there are also transformation centers, distributed with a uniform density n_0 , then the position of the maximum velocity tends towards smaller values of argument χ , and its value becomes slightly less. If the quantity a is small in comparison with n_0 , then the velocity maximum is determined by values of argument χ close to zero, and its magnitude is slightly different from the value $W_m = 1.285$.

In the converse situation, if to the transformation centers distributed with constant density n_0 are added

TABLE 5

centers formed in time, it is easy to obtain, using table 3, and the dependence $\theta = \tau \eta$, only in this case the parameter should be $1/\eta$.

In figure 4 the bold line represents curve (15), and the dashed line is the curve obtained from integral (2), expressed in dimensionless variables:

$$f(\tau) = \tau \left\{ 1 - \int_0^1 \exp \left[-\tau^2 \eta^2 (1-z)^2 - \tau^3 (1-z)^2 \right] (1+2z) dz \right\} \quad (27)$$

for $\tau \ll 1$

$$f(\tau) = \tau^2 \left[\frac{1}{2} \tau (1 - \frac{13}{32} \tau^3) + \frac{2}{3} \eta^2 (1 - \frac{2}{5} \tau^2 \eta^2 - \frac{13}{20} \tau^3) \right] \quad (28)$$

for $\tau \gg 1$

$$f(\tau) = \tau \left[1 - \frac{1}{2} \frac{1}{\tau^2 \eta^2} \left(1 - \frac{3}{2} \frac{1}{\tau \eta^4} + \frac{27}{4} \frac{1}{\tau^2 \eta^8} - \dots \right) \right] \quad (29)$$

and calculated for $\eta = 1$. In figure 5 the bold line is the curve of the velocity from (15), obtained from (23) for the values of the parameter $\eta = 0.5$ (first dashed curve) and $\eta = 1$, (the second dashed curve).

3. The experimental determination of the magnitudes of λ , n_0 , and a .

The entities λ and n_0 can be easily determined

experimentally. For an observed velocity of propagation of transformation, after an appreciable amount of time has elapsed since the beginning of the process, when already to all intents and purposes a plane front has been established, we will have

$$\lambda = \lim_{t \rightarrow \infty} w(t) .$$

The velocity in the initial period of the process enables us to determine n_0 , knowing λ ,

$$n_0 = \frac{1}{2\pi\lambda} \lim_{t \rightarrow 0} \frac{w(t)}{t^2} .$$

In the case when $n_0 = 0$, similarly we obtain a:

$$a = \frac{3}{2\pi\lambda^3} \lim_{t \rightarrow 0} \frac{w(t)}{t^3} .$$

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